(iii) We have tried to detect a special lability in the proximity of the amide group to the enol ether bond. Brief treatment (5 min) of the photoproduct III with methanolic HCl led only to V by etherification of the allylic hydroxyl. But on standing overnight with methanolic HCl at room temperature the lactam easily opened to a (rearranged) basic compound characterized by a hydrochloride (mp 118–124°), perchlorate (mp 163–165°), and N-trifluoroacetyl derivative (mp 125°), all containing a new chromophore ($\lambda\lambda_{max}$ 245 (ϵ 3370), 294 nm (ϵ 885)) on the structure of which we hope to report soon.

Studies with different solvents involving oxygen quenching point to a novel type of cage effect directing the *intra*- and *inter*molecular subsequent reactions of the photoexcited intermediates.

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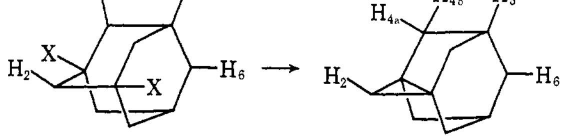
Tetracyclo[3.3.1.1^{3,7}.0^{1,3}]decane. A Highly Reactive 1,3-Dehydro Derivative of Adamantane

Sir:

The strain-free compound adamantane[1] (**1**, $C_{10}H_{16}$) can be converted to a reactive 1,3-dehydro derivative (**2**, $C_{10}H_{14}$) by inversion and bonding of two bridgehead positions. This highly strained hydrocarbon, tetracyclo[3.3.1.1^{3,7}.0^{1,3}]decane (**2**), possesses a cyclopropyl group which readily undergoes addition reactions to form a variety of mono- and disubstituted adamantanes.



1 **2**

Reaction of 1,3-dibromoadamantane[2] (**1**, X = Br) with a Na–K dispersion in refluxing heptane produces **2** accompanied by *ca.* 10% of adamantane. Moderate thermal stability of compound **2** is shown by its analysis and separation using gas–liquid partition chromatography (Carbowax columns at 150°, detector at 250°). Degassed solutions of **2** (0.04 *M* in heptane) are essentially unchanged after 3 days at 100°. However, even in dilute solutions at room temperature, reaction of **2** with air occurs promptly ($t_{1/2}$ = *ca.* 6 hr) and results in precipitation of peroxide containing material (white solid, explosion point *ca.* 160°).[3] The peroxide obtained from heptane solutions was reduced with $LiAlH_4$ to yield 1,3-dihydroxyadamantane (**1**, X = OH) as the major product. Analysis of the benzene-insoluble fraction from the peroxide precipitate corresponds to polymeric 1,3-dioxyadamantane, $[-O-C_{10}H_{14}-O-]_x$. *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.55; H, 8.28.

1,3-Dehydroadamantane in heptane solutions was further characterized by the following rapid reactions:[4] catalytic hydrogenation to yield greater than 92% adamantane, hydration with 1 *M* H_2SO_4 to 1-adamantanol, acetolysis to 1-adamantyl acetate, and bromination to 1,3-dibromoadamantane. Compound **2** is thus a readily available intermediate in the production of many bridgehead-substituted adamantanes; *e.g.*, titration of **2** with iodine in heptane produced 1,3-diiodoadamantane (**1**, X = I), mp 110–111°; nmr (benzene) δ 3.19 (H-2), 2.24 (H-4), 1.24 (H-5 and H-6). *Anal.* Calcd for $C_{10}H_{14}I_2$: C, 30.95; H, 3.64; I, 65.41. Found: C, 31.30; H, 3.71; I, 65.11.

Isolation of 1,3-dehydroadamantane by glpc gave an unstable crystalline solid with characteristic infrared absorptions at 3040 (cyclopropyl C–H stretching),[5] 2900, 1450, 1285, 1085, and 895 cm^{-1}. Its nmr spectrum (in degassed benzene) showed absorptions at δ 2.73 (broad singlet, two protons of H-5), 2.05 (triplet, J_{5-6} = 1.2 Hz, two protons of H-6), 1.66 (closely spaced multiplet for two protons of H-2), and a pair of doublets centered at 1.15 and 1.91 (for the four protons each of H-4a and H-4b, J_{ab} = 11 Hz). The large chemical-shift difference (0.76 ppm) of the geminal C-4 hydrogens is consistent with their positions above (H-4a) and nearer the side (H-4b) of the anisotropic cyclopropyl ring.[6] The protons on C-5 and C-6 lie in deshielded positions with respect to the cyclopropyl ring and they appear at unusually low fields.[7] *Anal.* Calcd for $C_{10}H_{14}$: mass, 134.1095. Found: mass, 134.1086 ± 0.001.

The great activity of 1,3-dehydroadamantane is no doubt due to its highly constrained structure and its relaxation to strainless adamantanes as the 1,3 bond is broken. Models suggest that compound **2** possesses car bon atoms (C-1 and C-3) with all four bonds almost extended from one side of each of these atoms. This rare[8] and unstable carbon configuration allows easy access to the approach of reagents from the other side. Inversion of atoms C-1 and C-3, with breakage of the weak internal cyclopropyl bond, completes the transformation to strain-free adamantyl structures.

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(3) In the presence of the free-radical inhibitor, 2,6-di-*t*-butyl-*p*-cresol, precipitation of peroxide does not occur and loss of **2** proceeds at a slower pace ($t_{1/2}$ = 30 hr with 3 × 10^{-2} *M* inhibitor).

(4) For some similar reactions of 2,4-dehydroadamantanes see A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Letters*, 1345 (1968); J. E. Baldwin and W. D. Fogelsong, *J. Am. Chem. Soc.*, **90**, 4303 (1968).

(5) H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966).

(6) The nonequivalent protons on C-4 of 1,3-disubstituted adamantanes ordinarily do not show different chemical shifts; see R. C. Fort, Jr., and P. von R. Schleyer, *ibid.*, **30**, 789 (1965).

(7) For some examples and references see J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).

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(9) Alfred P. Sloan Foundation Fellow.

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